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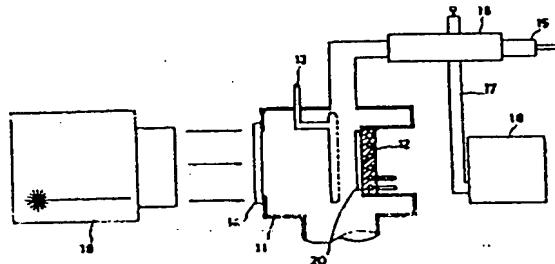
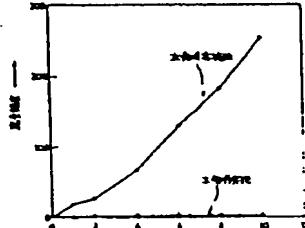
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TITLE : SURFACE TREATMENT



ABSTRACT : PURPOSE: To enhance the reliability of a wiring part by a method wherein an oxygen radical and hydrogen or water are made to act and the surface is oxidized in order prevent the wiring part from being corroded in a washing treatment after a treatment by using dilute hydrofluoric acid for removal of a fence.  
CONSTITUTION: The inside of a container 11 is evacuated in advance to produce a vacuum; oxygen is introduced into a discharge tube 15 at a flow rate of 30sc cm; on the other hand, hydrogen is introduced from a gas introduction pipe 13 connected to the container at a flow of 10sc cm; a pressure is kept at 0.4Torr; microwaves are applied; an electric discharge is generated. This treatment is executed for a 5minutes. A specimen whose fence has been removed by dilute HF after selective etching of an Al-Si-Cu alloy is exposed to an atmosphere of a mixed gas of oxygen (activated oxygen radical) and hydrogen; Al<sub>2</sub>O<sub>3</sub> can be formed on the surface of the Al-Si-Cu alloy. Accordingly, it is possible to prevent a wiring part composed of Al-Si-Cu from being corroded in a subsequent washing treatment. It is possible to eliminate a disconnection due to corrosion and to enhance the reliability of the wiring part.





European  
Patent Office

EUROPEAN SEARCH  
REPORT

Application Number

EP 89 11 0295

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
P,X	EP-A-0 305 946 (TOSHIBA K.K.) • Figure 3; column 5, lines 41-49; column 8, lines 15-37; claims 1-11; column 12, lines 17-41; figure 7 - - -	1-3,6,16	H 01 L 21/31		
P,A		4-5,7-16, 17-18			
P,A	EP-A-0 304 046 (FUJITSU) • Claims 1-6 - - -	1-5			
X	US-A-3 837 856 (SIGNETICS CORP.) • Column 3, line 3 - column 4, line 28; claims 1-3 - - -	1-3			
A		5,11-15			
X	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 134, no. 8, August 1987, pages 2045-2048, Manchester, NH, US; O. KROGH et al.: "Spectroscopic diagnostics of photoresist erosion in an aluminum etch plasma" • Page 2045, column 1, paragraph 2 - column 2, paragraph 1 - - -	1,3			
A		6-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
A	US-A-4 473 437 (TOSHIBA K.K.) • Claims 1-6 - - - -	11-15	H 01 L G 03 F		
The present search report has been drawn up for all claims					
Place of search	Date of completion of search	Examiner			
The Hague	13 November 90	VANCRAEYNEST F.H.			
CATEGORY OF CITED DOCUMENTS					
X: particularly relevant if taken alone	E: earlier patent document, but published on, or after the filing date				
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P: Intermediate document	&: member of the same patent family, corresponding document				
T: theory or principle underlying the invention					

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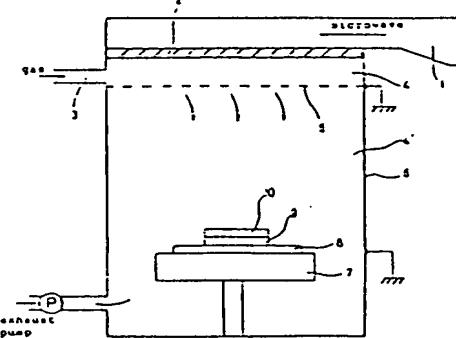
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(54) An ashing method for removing an organic film on a substance of a semiconductor device under fabrication.

(57) Plasma ashing methods, each for removing a resist material (10) formed on a ground layer (9) of a semiconductor device (8) under fabrication, are performed by using three kinds of reactant gases each composed of three different gases. The plasma ashing is performed: in an ashing rate of 0.5  $\mu\text{m}/\text{min}$  at 160 °C and with activation energy of 0.4 eV when a reactant gas composed of oxygen, water vapor and nitrogen is used; in an ashing rate of 0.5  $\mu\text{m}/\text{min}$  at 140 °C, with activation energy of 0.38 eV and without etching the ground layer (9) when a reactant gas composed of oxygen, water vapor and tetrafluoromethane is used; and in an ashing rate of 0.5  $\mu\text{m}/\text{min}$  at 140 °C, with activation energy of 0.4 eV when a reactant gas composed of oxygen, hy-

drogen and nitrogen is used.



## ASHING METHOD FOR REMOVING AN ORGANIC FILM ON A SUBSTANCE OF A SEMICONDUCTOR DEVICE UNDER FABRICATION

### GROUND OF THE INVENTION

#### Id of The Invention

The present invention relates to a removing method of an organic material used in a semiconductor device, and particularly the present invention relates to an ashing method of an organic film temporarily formed on a substance of a semiconductor device under fabrication.

In organic film such as a resist or a polyimide temporarily formed on a substance, which is a semiconductor device, for fabricating the semiconductor device was usually removed by an ashing method using oxygen plasma. Removing resist film is an important process in fabrication of semiconductor device, removing the resist as an organic film will be described, hereafter. Since the semiconductor device becomes very small as a Large Scale Integration device (LSI) or a Very Large Scale Integration circuit device (VLSI), the resist film, which is called simply the "resist" hereinafter, becomes hard to be removed by the usual ashing method using the oxygen plasma without damaging devices. Because, the property of the resist is changed during the process of ion implantation and etching, which are widely performed in the fabricating process of the LSI or the VLSI, so that a time is required for performing ashing, in other words, the ashing rate of the resist becomes small. In the resist is used many times in the fabricating process of the LSI or the VLSI, the ashing rate of each resist should be large to improve the throughput of the fabrication of the LSI or the VLSI. A layer, called simply a "ground layer" hereafter and the resist is formed thereon, is usually made of material such as silicon dioxide (SiO<sub>2</sub>), polysilicon (Si) or aluminum (Al). Generally, resist is not easy to be etched intentionally by the ashing method, in other words, the resist is to be etched precisely so as to be removed by the resist without damaging any of the ground layer in the ashing process. Therefore, when the ashing method is applied to the fabricating process of the LSI or the VLSI, great attention must be paid to leave the ground layer as it is. Because, the ground layer of the LSI or the VLSI is very thin and little part of it is not allowed to be etched. There are many kinds of plasma ashing methods for removing the resist film provided on a patterning layer in a semiconductor device, however, in all a down-flow ashing method is widely

used. Because, applying the down-flow ashing method to the plasma ashing process, damage caused by charged particles can be avoided producing. The down stream ashing rate generally depends on a temperature, which will be called an "ashing temperature" hereinafter, of the resist so that the ashing rate decreases with the decrease of the ashing temperature. The ashing rate is usually expressed by the well known Arrhenius plot by which the ashing rates are plotted in a line against the inverse numbers of the respective ashing temperatures. In the Arrhenius plot, the gradient of the line gives the activation energy for ashing in such that when the ashing rate decreases rapidly with the decrease of the ashing temperature, the activation energy is large, and when the ashing rate changes only little with the decrease of the ashing temperature, the activation energy is small. On this, the small activation energy is desirable because the ashing can be performed almost independently on the ashing temperature, in other words, the ashing can be performed in stable and precisely.

Recently, there is a tendency that a wafer process in the fabrication process of a semiconductor device is performed at a lower temperature according as the semiconductor device has a higher integration circuit as seen in the LSI or the VLSI. The ashing process is desired to be performed lower than 300°C, most preferably lower than 200°C to avoid contamination from the resist. In order to maintain a large ashing rate at a low temperature, larger than 0.5 μ/min for practical use, the activation energy of the ashing rate must be also small. The activation energy of the ashing rate can be changed to some extent by changing the species of reactant gases used for ashing. The selection and the combination of the reactant gases are very important for making the ashing rate high and the activation energy small and for etching the resist precisely, leaving the ground layer as perfectly as possible and for minimizing damage. The selection and the combination of the reactant gases has been studied energetically.

#### (2) Description of The Related Art

The downstream ashing is performed in a downstream of a microwave plasma using a microwave plasma resist stripper. This is fully disclosed in the paper titled "Heavy Metal Contamination From Resists during Plasma Stripping" by Shuzo Fujimura and Hiroshi Yano, in Elect. Chem. Soc. Vol. 135, No. 5, May 1988.

The downstream of a microwave plasma resist stripper consists of a vacuum chamber including a plasma generating chamber, a vacuum pump for exhausting gas in the vacuum chamber, a process chamber including a pedestal on which a sample wafer is placed and a microwave power source. A reactant gas is supplied to the process chamber through the plasma generating chamber.

Then, a reactant gas plasma is generated in the plasma generating chamber by the microwaves, so that active species for ashing produced in the gas plasma flows down to the process chamber and reacts with a resist previously formed on the sample wafer so as to remove the resist.

In the downstream ashing process, oxygen has been used as the reactant gas for a long time as described before. However, when only oxygen is used, the ashing rate is small and the activation energy is large, so that the downstream ashing using only oxygen was hard to be applied to the fabricating process of the LSI or the VLSI. Therefore, many other reactant gases have been studied for increasing the ashing rate and decreasing the activation energy, by adding other kinds of gases to the oxygen. As a result, several kinds of effective reactant gases have been found as will be described below, giving four examples, a first, a second, a third and a fourth examples, tracing the development of the reactant gases. The ashing rate and the activation energy are related to removing the resist film provided in a semiconductor device by plasma ashing method, hereinafter.

A first reactant gas was a mixed gas of oxygen ( $O_2$ ) with a halogenide gas such as tetrafluoromethane ( $CF_4$ ). The first reactant gas was most commonly used because it had a large ashing rate. Fig. 1 shows the ashing rate for commercially available photoresist (OFPR-800, TOKYO-OHKA) plotted against the variation of flow ratio of tetrafluoromethane to the mixed gas at room temperature. The ashing rate in the case using a reactant gas is simply called the ashing rate with the reactant gas, hereinafter. In Fig. 1, when tetrafluoromethane is added to oxygen as much as about 15% in the flow ratio, the ashing rate reaches a maximum value, 1.5  $\mu\text{m}/\text{min}$  at 25 °C, being large enough for practical use. However, the ground layer such as  $SiO_2$ , polysilicon (Si) or Al is etched because of fluorine (F) mixed in the first reactant gas. On the other hand, when the first reactant gas is used, the activation energy is drastically reduced to a value of 0.1 eV from 0.52 eV which is the activation energy with only oxygen. Such large decrease of the activation energy is due to the tetrafluoromethane, which was explained in the paper, J.J.Hannon and J.M.Cook, J. Electrochem. Soc., Vol. 131, No. 5, pp 1164 (1984).

A second reactant gas was a mixed gas of

oxygen and nitrogen ( $N_2$ ), not containing fluorine (F), which did not etch the ground layer. The ashing rate and the concentration of oxygen atom in a down-flowed gas were measured by varying the flow ratio of nitrogen to the second reactant gas as shown in Fig. 2; wherein, the concentration of oxygen atom was measured by an actinometry method. In this case, the ashing temperature was 200 °C and the flow rate of the second reactant gas was 1000 Standard Cubic Centimeter per Minute (SCCM). In Fig. 2, white circles represent the concentrations of oxygen atom, obtained from the spectral intensity ratio of the radiation from an oxygen atom (at a wavelength of 6158 Å) to the radiation from an argon atom (at a wavelength of 7067 Å) and triangles represent the concentrations of the same oxygen atom, obtained from the spectral intensity ratio of the radiation from an oxygen atom (at a wavelength of 4368 Å) to the radiation from an argon atom (at a wavelength of 7067 Å). Further, the values of these concentrations are normalized by a maximum of the values of the concentrations, positioned at about 10% of the flow ratio of nitrogen to the second reactant gas. Multiplication signs represent the ashing rates to the flow ratio of nitrogen to the second reactant gas. As can be seen from Fig. 2, the curve of the ashing rate and that of the concentration of oxygen atom are coincided each other, which means that oxygen atoms are only effective in performing the ashing. Fig. 3 shows the Arrhenius plot of the ashing rate when the second reactant gas contains 90% of oxygen and 10% of nitrogen in the flow ratio and the Arrhenius plot of the oxygen gas only. The ashing temperature is denoted by T. The ashing rate of the second reactant gas is plotted by a circle and the ashing rate of the oxygen is plotted by a multiplication sign. The ashing rate with the second reactant gas is about two times of that of oxygen only. The activation energy of ashing in the case using a reactant gas is simply called the activation energy of the reactant gas, hereinafter. The activation energy ( $E_a$ ) of the second reactive gas, and that of the oxygen are equally 0.52 eV. That is, the activation energy does not change by mixing nitrogen. The ashing rate of the second reactive gas of 0.2  $\mu\text{m}/\text{min}$  at 160 °C is too small for practical use. In order to increase the ashing rate, another kind of gas was needed.

The third reactant gas was a mixed gas of oxygen and water vapor ( $H_2O$ ) which did not etch the ground layer. The ashing rate and concentration of oxygen atom were measured by varying the flow ratios of water vapor to the third reactant gas as shown in Fig. 4. The measurements were performed under 180 °C ashing temperature and 1000 SCCM flow rate of the third reactant gas. Circles and multiplication signs in Fig. 4 represent the

same as in Fig. 2 respectively. When the flow ratio of water vapor to the third reactant gas exceeds 40%, the concentration of the oxygen atom decreases with the increase of the water vapor flow ratio. However, the ashing rate does not decrease so much as the decrease of the concentration of oxygen atom as seen in Fig. 4. This means that some active species except oxygen atoms are possible to take part in the ashing. Fig. 5 compares the Arrhenius plot of the third reactant gas containing 60% of oxygen and 40% of water vapor and Arrhenius plot of the oxygen gas. The ashing rate of the third reactant gas having 40% flow ratio of water vapor is plotted by triangles and the ashing rate of the oxygen is plotted by multiplication signs. The activation energy of the third reactive gas is 0.39 eV which is about three quarter of the activation energy (0.52 eV) of oxygen as shown in Fig. 6. Fig. 6 shows the activation energy of the ashing in the case using the third reactant gas by varying the flow ratios of water vapor to the third reactant gas, by white circles. In Fig. 6, the activation energy of ashing in the case using the mixed gas of oxygen and hydrogen by varying the flow ratio of hydrogen to the mixed gas is shown by solid circles, for the sake of comparison. It is seen in Fig. 6 that the activation energy is easily reduced by adding water vapor a little and the activation energy is constant independently on the flow ratio of water vapor when the flow ratio of water vapor exceeds 5%. The activation energy of the second reactant gas is also indicated by a dot chain line in Fig. 6 for the comparison with the third reactant gas. It is seen from this comparison that the activation energy does not change by adding nitrogen to oxygen. The behavior similar to the mixed gas of oxygen and water vapor is seen for the mixed gas of oxygen and hydrogen. On the other hand, the ashing rate of the third reactant gas is about  $0.22 \mu\text{m}/\text{min}$  at  $160^\circ\text{C}$ , as seen in Fig. 5. In conclusion, the value of the ashing rate of the third reactant gas is still too small for practical use.

The fourth reactant gas is a mixed gas of oxygen, nitrogen and tetrafluoromethane. The fourth reactant gas is disclosed in the Japanese laid-open patent application, SHO 63-102232, titled "DRY ETCHING APPARATUS" by Mikio Nonaka. When the flow ratio of tetrafluoromethane and nitrogen are in the range of 5 to 20% and 5 to 10% respectively, the large ratio of a rate of etching a positive resist to a rate of etching a ground layer is obtained without decreasing the ashing rate. However, the etching of ground layer can not be avoided occurring in this case.

A mixed gas made by adding as little as 0.2% of hydrogen to a mixed gas of oxygen, nitrogen and tetrafluoromethane is commercially available from EMERGENT TECHNOLOGIES CO.(Phoenix

2320 NORD Photoresist Stripper). In this case, the hydrogen diluted by nitrogen is added in order to improve matching with microwave power. That is, the adding hydrogen to the mixed gas is not for reduction of the activation energy. So, the mixed gas is essentially the same as the first reactant gas. In fact, it is also known that the activation energy of the second reactant gas mixed with hydrogen does not decrease until up to 0.5% of hydrogen.

As seen from the description of the first, second, third and fourth reactant gases, an ideal mixed gas, having a large ashing rate and small activation energy and never etching the ground layer, has not been found although much has been studied on new reactant gases.

#### SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to improve the ashing process for removing the organic film formed on the ground layer of the semiconductor device under fabrication, so that the ashing rate increases, the activation energy decreases and the ground layer is never etched in the ashing process.

The above object is achieved by applying a reactant gas composed of at least three kinds of gases to the ashing process. The reactant gas is separated into two group mixed gases one (a first group gas) of which is composed of at least oxygen and water vapor and the other (a second group gas) of which is composed of at least oxygen and hydrogen. As well known, oxygen in each group gas is a main gas for performing the ashing, however water vapor in the first group gas and hydrogen in the second group gas are for mainly decreasing the activation energy, increasing the ashing rate and avoiding the ground layer being etched in cooperation with another third gas respectively added to the first group gas and the second group gas. The third gas added to the first group gas is hydrogen, nitrogen, nitrogen oxide or halogenide and that added to the second group gas is water vapor, nitrogen, nitrogen oxide or halogenide. The halogenide includes tetrafluoromethane( $\text{CF}_4$ ), chlorine( $\text{Cl}_2$ ), nitrogen trifluoride( $\text{NF}_3$ ), hexafluoroethane( $\text{C}_2\text{F}_6$ ) and trifluoromethane( $\text{CHF}_3$ ). The flow rate of the water vapor and the third gas of the first group gas and that of the hydrogen and the third gas of the second group gas are controlled respectively.

In the first group gas including the third gas of nitrogen, the water vapor added to oxygen has the same effect of that described in reference to Fig. 5, and the added nitrogen has the same effect of that described in reference to Fig. 3. However, in the

first group gas including the third gas of nitrogen, these added water vapor and nitrogen produce a synergistic effect on increasing the ashing rate and decreasing the activation energy. That is, it was simply assumed from Figs. 3 and 5 that the ashing rate of the first group gas including the third gas of nitrogen would increase in the same way as the case of a gas only mixing oxygen and nitrogen and the activation energy of the first group gas including the third gas of nitrogen would decrease in the same way as the case of a gas only mixing oxygen and water vapor. However, actually, the ashing rate increases as much as two times of the assumed value from Fig. 3 though the activation energy decreases to a value approximately same of the value assumed from Fig. 5.

The first group gas including the third gas of halogenide such as tetrafluoromethane is excellent as the reactant gas. Recently, halogenide has not been used as the third gas in the fabrication of the LSI or the VLSI because of disadvantage that halogen easily etches the ground layer. However, according to the experiment by the inventors, it is found that the first group gas including the third gas of halogenide does not etch the ground layer when the water vapor is included in the reactant gas, supplied by a flow ratio controlled so as to exceed a designated value. Because, the halogen atoms react to the hydrogen atoms of the water molecules. As the result, the action of the halogen is suppressed. Using the first group gas including the third gas of halogen as the reactant gas, the ashing rate becomes large and the activation energy of the ashing rate becomes small, compared with the first group gas including the third gas of nitrogen.

As the second group gas including the third gas of nitrogen is discussed. According to the experiment by the inventors, the activation energy is decreased to 0.44 eV from 0.52 eV by adding hydrogen of more than 3%; wherein 0.52 eV is the activation energy corresponding to the oxygen. This is because of that the hydrogen acts to decrease the activation energy. The ashing rate of the second group gas including the third gas of nitrogen is large as much as two or three times of that of the usual mixed gas of oxygen and nitrogen.

These mixed gases, described above, of the first group gas including nitrogen as the third gas, the first group gas including halogenide as the third gas and the second group gas have three advantages of having a large ashing rate, having small activation energy and etching no ground layer in the fabrication process of the LSI or the VLSI.

Fig. 1 is a graph showing the variation of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$  and  $CF_4$  with the flow ratio of  $CF_4$  to the reactant gas, at 25°C ashing temperature.

Fig. 2 is a graph showing the variation of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$  and  $N_2$  at 200°C ashing temperature and the variation of the concentration of oxygen atom in a down-flowed gas with the flow ratio of  $N_2$  to the reactant gas.

Fig. 3 is a graph showing Arrhenius plots of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$  having 90% flow ratio,  $N_2$  having 10% flow ratio and the reactant gas composed of oxygen.

Fig. 4 is a graph showing the variation of the ashing rate in the case of using the reactant gas composed of  $O_2$  and  $H_2O$  at 180°C ashing temperature and the variation of the concentration of oxygen atom in a down-flowed gas with the flow ratio of  $H_2O$  to the reactant gas.

Fig. 5 is a graph showing Arrhenius plots of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$  having 60% flow ratio,  $H_2O$  having 40% flow ratio and the reactant gas composed of oxygen.

Fig. 6 is a graph showing the variation of the activation energy of the ashing using the reactant gas composed of  $O_2$  and  $H_2O$  with the flow ratio of  $H_2O$  to the reactant gas.

Fig. 7 is a schematical drawing of a vacuum chamber of a down-flow ashing apparatus.

Fig. 8 is a graph, represented in Arrhenius plots, showing the ashing rates for resist in the case of using different kinds of reactant gases.

Fig. 9 is a graph showing the variations of the ashing rate in the case of using the reactant gas composed of  $O_2$ ,  $H_2O$  and  $N_2$  at 180°C and 200°C ashing temperature with the flow ratio of  $N_2$  to the mixed gas of  $O_2$  and  $N_2$ , where the flow rate of  $H_2O$  is kept in constant.

Fig. 10 is a graph showing variations of the rate of etching  $SiO_2$  layer at 150°C and 25°C ashing temperature with flow ratio of  $H_2O$  to the mixed gas, in the case of performing the plasma ashing using the reactant gas composed of  $O_2$ ,  $H_2O$  and  $CF_4$ .

Fig. 11 is a graph showing the variations of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$ ,  $H_2O$  and  $CF_4$  at 25°C, 150°C and 180°C ashing temperature with flow ratio of  $H_2O$  to the reactant gas, where 15% flow ratio of  $CF_4$  to the mixed gas of  $O_2$  and  $CF_4$  is kept.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 12 is a graph showing Arrhenius plots of the ashing rate for resist in the case of using the reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$ , the reactant gas composed of  $O_2$  and  $N_2$  and the reactant gas composed of oxygen.

Fig. 13 is a graph showing the variations of the activation energy of the ashing using the reactant gas composed of  $O_2$  and  $H_2O$  and the reactant gas composed of  $O_2$  and  $H_2$ , with the flow ratio of  $H_2O$  to the reactant gas of  $O_2$  and  $H_2O$  and with the flow ratio of  $H_2$  to the reactant gas of  $O_2$  and  $H_2$  respectively.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The plasma ashing methods of removing the resist, using three kinds of reactant gases will be described as the embodiments of the present invention, in reference to Figs. 8 to 12. The embodiments are separated into three, a first, a second and a third embodiment, in accordance with the three kinds of the reactant gases. The plasma ashing are performed by a down flow ashing method using a conventional downstream microwave plasma resist stripper schematically shown in Fig. 7.

##### The First Embodiment

The first embodiment is the plasma ashing method using a reactant gas composed of  $O_2$ ,  $H_2O$  and  $N_2$ . In Fig. 7, the reactant gas composed of 720 SCCM  $O_2$ , 100 SCCM  $H_2O$  and 180 SCCM  $N_2$  is supplied to an initially exhausted vacuum chamber 6 through a gas inlet 3, keeping the gas pressure in the vacuum chamber 6 at about 0.8 Torr. The flow rates of the gases of  $O_2$ ,  $H_2O$  and  $N_2$  are controlled respectively by a controller, not depicted, before the gases flow into the vacuum chamber 6. Through a wave guide 1 and a window 2, microwave power of 2.45 GHz is supplied into a plasma generating chamber 4. Plasma is generated with the reactant gas in the plasma generating chamber 4 and the charged particles in the plasma are trapped by a shower plate 5. Then, only neutral active species, generated in the plasma, flow down to a process chamber 4' through the holes provided in a showerhead plate 5 and touch a surface of a resist 10 formed on a ground layer 9 of a sample wafer 8 placed on a stage 7 heated at 140°C by a heater not depicted. As a result, the resist 10 is etched until the surface of the ground layer 9 appears without etching any part of the ground layer. Because the reactant gas does not contain halogen, the ground layer 9 is never

etched.

The ashing rate in the case of using the reactant gas composed of  $O_2$ ,  $H_2O$  and  $N_2$  is shown by a line connecting white triangles in Fig. 8 represented in Arrhenius plot. In Fig. 8, the ashing rates in the case of using other several kinds of reactant gases are also shown in the same way, for the sake of comparison. That is, the ashing rate in the case of using the reactant gas composed of only  $O_2$ , that of using the reactant gas composed of  $O_2$  and  $H_2O$  and that of using the reactant gas composed of  $O_2$  and  $N_2$  are shown by solid circle, solid triangle and white circle respectively. As seen in Fig. 8, the ashing rate in the case of using the reactant gas of  $O_2$ ,  $H_2O$  and  $N_2$  is larger than the ashing rate in the cases of using the reactant gas composed of only  $O_2$ , of  $O_2$  and  $H_2O$ , and of  $O_2$  and  $N_2$ . The reactant gas composed of  $O_2$ ,  $H_2O$  and  $N_2$  has the ashing rate of 0.5  $\mu\text{m}/\text{min}$  at 180°C ashing temperature and the activation energy of 0.4 eV. For practical use, the 0.5  $\mu\text{m}/\text{min}$  ashing rate is large enough and the 0.4 eV activation energy is small enough. Fig. 9 shows the variation of the ashing rate for the various flow ratios of  $N_2$  to the mixed gas of  $O_2$  and  $N_2$ , at the ashing temperature of 180°C and that of 200°C, keeping the flow rate of  $H_2O$  in 100 SCCM and the total flow rate of  $O_2$  and  $N_2$  in 900 SCCM. It can be seen in Fig. 9 that the ashing rate in the case of using the reactant gas composed of  $O_2$ ,  $H_2O$  and  $N_2$  is hardly changed by varying the flow ratio of nitrogen to the mixed gas of  $O_2$  and  $N_2$  when the flow ratio is larger than 5%. Therefore, the reactant gas of mixing  $O_2$ ,  $H_2O$  and  $N_2$  having the flow ratio larger than 5% can be also used as the reactant gas for performing a precise ashing process.

The flow rate of each component gas is set 720 SCCM, 100 SCCM and 180 SCCM for  $O_2$ ,  $H_2O$  and  $N_2$ , respectively, as a desirable example. However flow rate of  $N_2$  is not limited if the flow ratio of  $N_2$  to the mixed gas of  $O_2$  and  $N_2$  is larger than 5%, because the ashing rate is constant regardless of the flow ratio when the flow ratio exceeds 5% as seen in Fig. 9. The flow rate of  $H_2O$  is not limited if the flow ratio of  $H_2O$  to the mixed gas of  $O_2$  and  $H_2O$  is larger than 1%, because the activation energy is about 0.4 eV regardless of the flow ratio when the flow ratio exceeds 1%, as seen in Fig. 6.

In the first embodiment,  $NO_x$  or  $H_2$  can be added to the mixed gas of  $O_2$  and  $H_2O$  instead of  $N_2$ .

##### The Second Embodiment

In the second embodiment, the reactant gas composed of  $O_2$ ,  $H_2O$  and  $CF_4$  is used for the plasma ashing. The ashing is performed in the

same way as described in the first embodiment. The flow rates of  $O_2$ ,  $H_2O$  and  $CF_4$  are 730 SCCM, 150 SCCM and 120 SCCM, respectively.

The disadvantage of etching the ground layer by using  $CF_4$  can be avoided occurring when the flow ratio of  $H_2O$  to the reactant gas is controlled so as to be larger than 10% as shown in Fig. 10. Fig. 10 is a graph showing the etching rate, at 150°C and 25°C ashing temperature, of a ground layer made of  $SiO_2$ , with the flow ratio of  $H_2O$  to the reactant gas, under a condition that the total flow rate of  $O_2$ ,  $H_2O$  and  $CF_4$  is kept in 1000 SCCM and the flow ratio of  $CF_4$  to the mixed gas of  $O_2 + CF_4$  is kept in 15%. From Fig. 10, it can be seen that when the flow ratio of  $H_2O$  to the reactant gas exceeds 10%, the etching rate of the ground layer of  $SiO_2$  becomes zero, in other words, the ground layer of  $SiO_2$  is never etched. Thus, this 10% of the  $H_2O$  ratio is a very important percentage to avoid the ground layer being etched. Incidentally, when the  $H_2O$  ratio to the reactant gas is 10%, it can be calculated from the above condition in Fig. 10 that the flow ratios of  $O_2$  and  $CF_4$  to the reactant gas are 76.5% and 13.5% respectively.

The ashing rate of the reactant gas composed of  $O_2$ ,  $H_2O$  and  $CF_4$  is shown by a line connecting reversed solid triangles in Fig. 8. As shown in Fig. 8, the ashing rate is the largest, compared with other ashing rates in the cases of using other reactant gases.

The ashing rate of the reactant gas composed of  $O_2$ ,  $H_2O$  and  $CF_4$  was measured by varying the flow ratio of  $H_2O$  to the reactant gas at 25°C, 150°C and 180°C ashing temperature respectively, under a condition that the total flow rate of  $O_2$ ,  $H_2O$  and  $CF_4$  was kept in 1000 SCCM and the flow ratio of  $CF_4$  to the mixed gas of  $O_2$  and  $CF_4$  was kept in 15%. The results of the measurement are shown in Fig. 11 where it can be seen that when the flow ratio of  $H_2O$  to the reactant gas exceeds 10%, the ashing rate is constant and independent of flow ratio of  $H_2O$  to the reactant gas.

The flow rate of each component gas is set 730 SCCM, 150 SCCM and 120 SCCM for  $O_2$ ,  $H_2O$  and  $CF_4$ , respectively, as a desirable example. However flow rate of  $H_2O$  is not limited if the number of hydrogen atoms of  $H_2O$  is larger than the number of fluorine atoms liberated from  $CF_4$ . On the other hand, the flow ratio of  $H_2O$  to the mixed gas of  $O_2$  and  $H_2O$  must be larger than 1%, so that the activation energy of ashing in the case of using the reactant gas is about 0.4 eV regardless of the flow ratio, as seen in Fig. 6.

In the second embodiment,  $CF_4$  is used as a halogenide, however  $Cl_2$ ,  $NF_3$ ,  $C_2F_6$  and  $CHF_3$  can be used instead of  $CF_4$ .

### The Third Embodiment

The third embodiment is the plasma ashing method using a reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$ . That is, the reactant gas composed of 720 SCCM  $O_2$ , 100 SCCM  $H_2$  and 180 SCCM  $N_2$  is applied to the down flow ashing process as described in the first embodiment.

In the case of using the reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$ , the ashing rate is shown by a line connecting white squares in Fig. 12 represented in Arrhenius plot, and the activation energy is shown with the flow rate of  $H_2$  to the reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$  in Fig. 13.

In Fig. 12, the ashing rate in the case of using a reactant gas composed of only  $O_2$  and that of using a reactant gas composed of  $O_2$  and  $N_2$  are also shown by a line connecting multiplication signs and a line connected white circles respectively, for the sake of the comparison with the reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$ . In the case of using the reactant gas composed of  $O_2$ ,  $H_2$  and  $N_2$ , the ashing rate is about 0.7  $\mu m/min$  at 160°C of ashing temperature as shown in Fig. 12, and the activation energy is about 0.4 eV as shown in Fig. 13.

In Fig. 13, it is found that the activation energy rapidly decreases to a value of approximately 0.4 eV during the flow ratio is increased from 0% to approximately 5% and kept constantly in the value more or less than 0.4 eV in a region of the flow ratio beyond 5%. The plasma ashing is actually carried out in this constant region of the activation energy. In Fig. 13, it can be said that the characteristic of having the constant activation energy is very important for performing the plasma ashing in stable and precisely.

The flow rate of each component gas is set 720 SCCM, 100 SCCM and 180 SCCM for  $O_2$ ,  $H_2$  and  $N_2$ , respectively, as a desirable example. However, the flow rate of  $H_2$  is not limited if the flow ratio of the  $H_2$  the reactant gas is larger than 3%, because the activation energy of ashing in the case using the reactant gas is about 0.4 eV regardless of the flow ratio, as seen in Fig. 13. The flow rate of  $N_2$  is not limited if the flow ratio of  $N_2$  to the mixed gas of  $O_2$  and  $N_2$  is larger than 5%, because the ashing rate is constant regardless of the flow ratio when the flow ratio exceeds 5%, as seen in Fig. 9.

In the third embodiment, the plasma ashing is performed by using the reactant gas of  $O_2$ ,  $H_2$  and  $N_2$ . However, it was confirmed that  $H_2O$ ,  $NO_x$  or halogenide can be used instead of  $N_2$ .

The first, second and third embodiments described above are related to removing the resist film by plasma ashing, however the present invention can be applied to removing the organic poly-

mer film.

Though the reactant gases described in the first, second and third embodiments are composed of three kinds of gases, an inert gas such as He, Ne or Ar can be added to the reactant gases up to 7%.

### Claims

1. A ashing method for removing an organic material formed on a ground substance of a semiconductor device (8), said method comprising the steps of:

providing ashing means for performing the removal of the organic material by using a reactant gas plasma;

supplying a mixed gas consisting essentially of oxygen, water vapor and a first additional gas to said plasma ashing means;

controlling flow ratios of the oxygen, the water vapor and the first additional gas of said mixed gas for obtaining a first reactant gas with which the plasma ashing is performed in a ashing rate larger than and with activation energy at most equal to, those respectively in the case of using the reactant gas composed of oxygen and water vapor;

generating plasma of the first reactant gas for producing active species of the first reactant gas; and removing the organic material by using the active species, leaving the ground substance.

2. A method according to claim 1, wherein said removing step is performed in down stream from the plasma.

3. A method according to claims 1 or 2, wherein the first additional gas is selected from the group consisting of hydrogen, nitrogen and nitrogen oxide.

4. A method according to claim 3, wherein said flow ratios of the oxygen, the water vapor and the first additional gas selected to the nitrogen of the mixed gas is controlled so that a flow ratio of the water vapor to a gas composed of the oxygen and the water vapor is set so as to be more than 1% and a flow ratio of the nitrogen to a gas composed of the oxygen and the nitrogen is set so as to be more than 5%.

5. A method according to claim 4 further comprising the step of setting a temperature of the organic material at higher than 160°C, so as to obtain an ashing rate larger than 0.5 μm/min.

6. A plasma ashing method for removing an organic material formed on a ground substance of a semiconductor device (8), said method comprising the steps of:

providing plasma ashing means for performing the removal of the organic material by plasma ashing, using a reactant gas;

supplying a mixed gas consisting essentially of oxygen, water vapor and a second additional gas to said plasma ashing means;

controlling flow ratios of the oxygen, the water vapor and the second additional gas of said mixed gas for obtaining a second reactant gas with which the plasma ashing is performed in a ashing rate larger than and with activation energy at most equal to, those respectively in the case of using the reactant gas composed of oxygen and water vapor, and without etching the ground substance;

generating plasma of the second reactant gas for producing active species of the second reactant gas; and

removing the organic material by using the active species, without etching the ground substance.

7. A method according to claim 6, wherein said removing step is performed in down stream from the plasma.

8. A method according to claims 6 or 7, wherein the second additional gas is selected from a halogenide group consisting of tetrafluoromethane, chlorine, nitrogen trifluoride, hexafluoroethane and trifluoromethane.

9. A method according to claim 8, wherein said flow ratios of the oxygen, the water vapor and the second additional gas selected to tetrafluoromethane is controlled so that a flow ratio of the water vapor to a gas composed of the oxygen and the water vapor is set so as to be more than 1% and a flow ratio of the tetrafluoromethane to a gas composed of the water vapor and the tetrafluoromethane is set so that a number of hydrogen atoms is greater than a number of halogen atoms.

10. A method according to claim 9 further comprising the step of setting a temperature of the organic material at higher than 140°C, so as to obtain an ashing rate larger than 0.5 μm/min.

11. A plasma ashing method for removing an organic material formed on a ground substance of a semiconductor device (8), said method comprising the steps of:

providing plasma ashing means for performing the removal of the organic material by plasma ashing, using a reactant gas;

supplying a mixed gas consisting essentially of oxygen, hydrogen which is larger than 1% of the mixed gas and a third additional gas to said plasma ashing means;

controlling flow ratios of the oxygen, the hydrogen and the third additional gas of said mixed gas for obtaining a third reactant gas with which the plasma ashing is performed in a ashing rate larger than and with activation energy at most equal to, those respectively in the case of using the reactant gas composed of oxygen and hydrogen;

generating plasma of the third reactant gas for

producing active species of the third reactant gas;  
and  
removing the organic material by using the active  
species, leaving the ground substance.

12. A method according to claim 11, wherein  
said removing step is performed in down stream  
from the plasma. 5

13. A method according to claims 11 or 12,  
wherein the third additional gas is selected from  
the group consisting of nitrogen and nitrogen oxide. 10

14. A method according to claim 13, wherein  
said flow ratios of the oxygen, the water vapor and  
the third additional gas selected to the nitrogen is  
controlled so that a flow ratio of the hydrogen to a  
gas composed of the oxygen, the hydrogen and  
the nitrogen is set so as to be more than 3% and a  
flow ratio of the nitrogen to a gas composed of the  
oxygen and the nitrogen is set so as to be more  
than 5%. 15

15. A method according to claim 14 further  
comprising the step of setting a temperature of the  
organic material at higher than 140 °C, so as to  
obtain an ashing rate larger than 0.5 µm/min. 20

16. A plasma ashing method for removing an  
organic material formed on a ground substance of  
a semiconductor device (8), said method comprising  
the steps of: 25

providing plasma ashing means for performing the  
removal of the organic material by plasma  
ashing, using a reactant gas; 30

supplying a mixed gas consisting essentially of  
oxygen, hydrogen and a fourth additional gas to  
said plasma ashing means; 35

controlling flow ratios of the oxygen, the hydrogen  
and the fourth additional gas of said mixed gas for  
obtaining a fourth reactant gas with which the plasma  
ashing is performed in a ashing rate larger than  
and with activation energy at most equal to, those  
respectively in the case of using the reactant gas  
composed of oxygen and hydrogen, and without  
etching the ground substance; 40

generating plasma of the fourth reactant gas for  
producing active species of the fourth reactant gas;  
and 45

removing the organic material by using the active  
species, without etching the ground substance.

17. A method according to claim 16, wherein  
said removing step is performed in down stream  
from the plasma. 50

18. A method according to claims 16 or 17,  
wherein said fourth additional gas is selected from  
a halogenide group consisting of  
tetrafluoromethane, chlorine, nitrogen trifluoride,  
hexafluoroethane and trifluoromethane. 55

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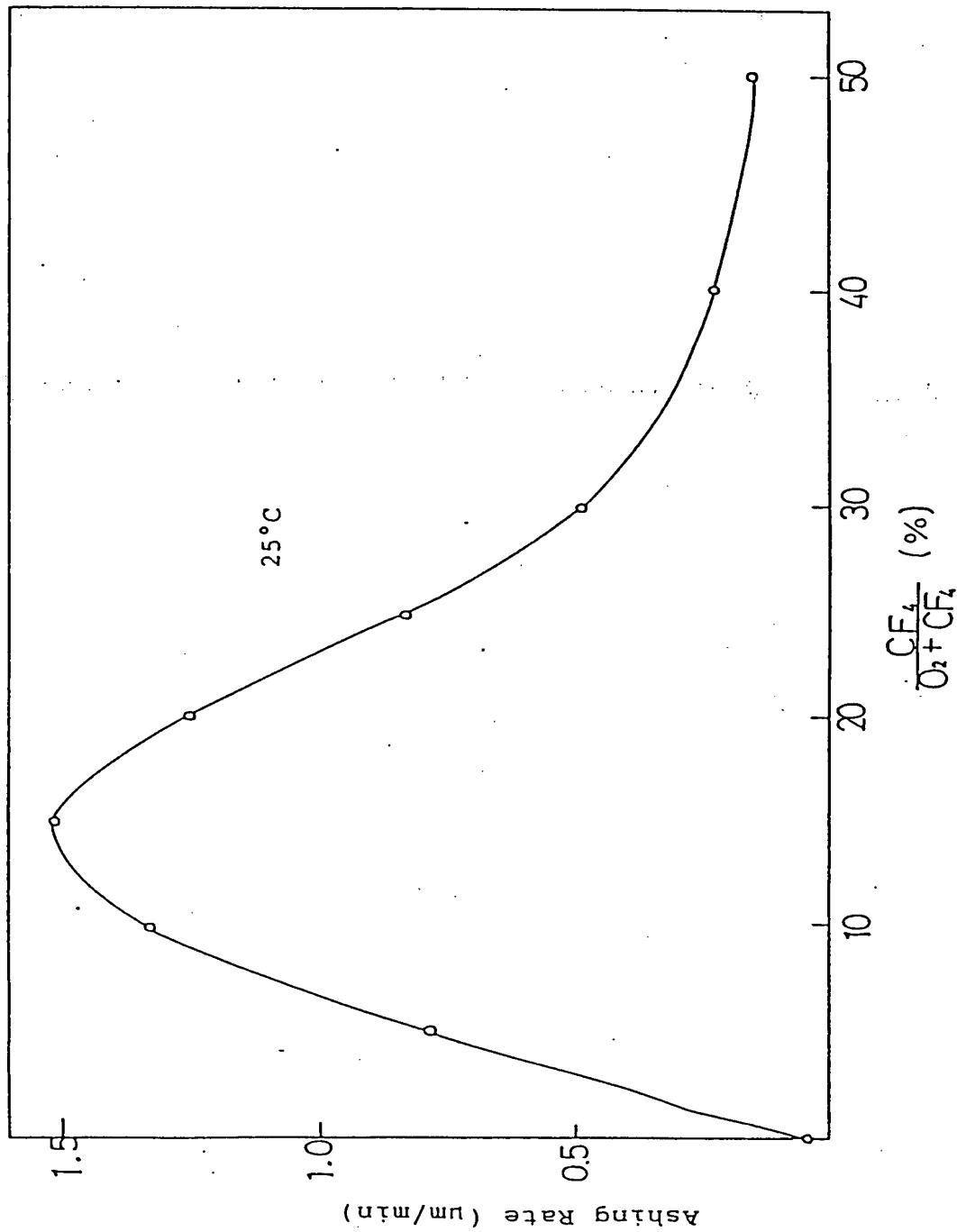


FIG. 1

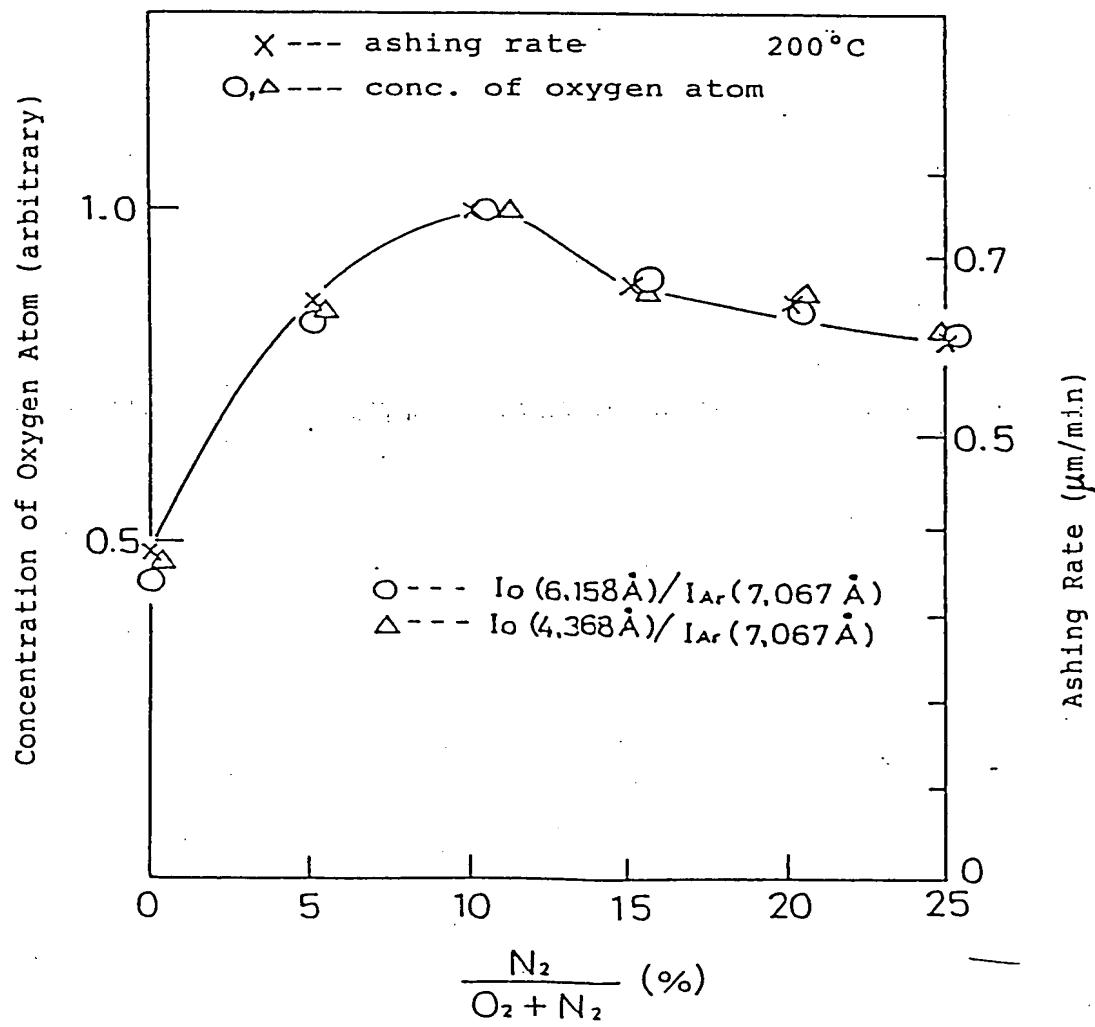


FIG. 2

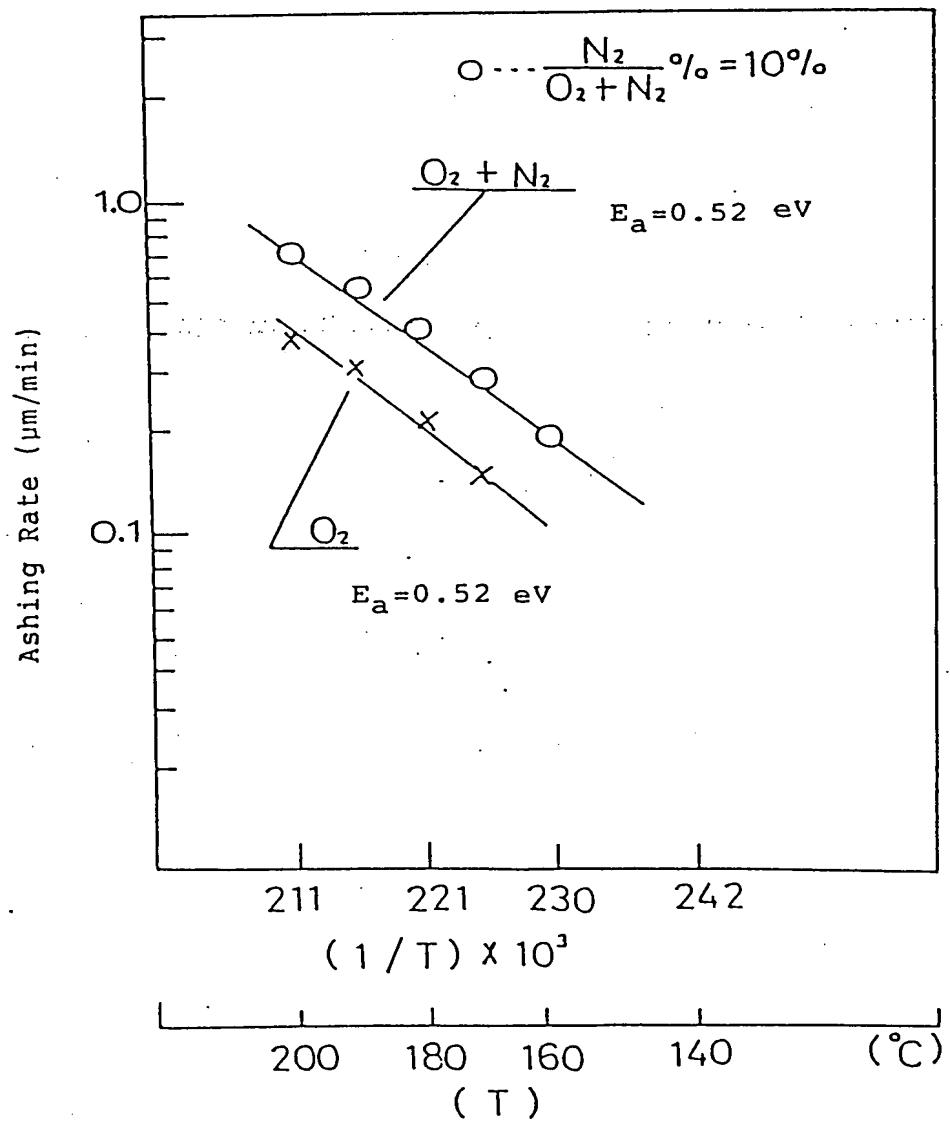
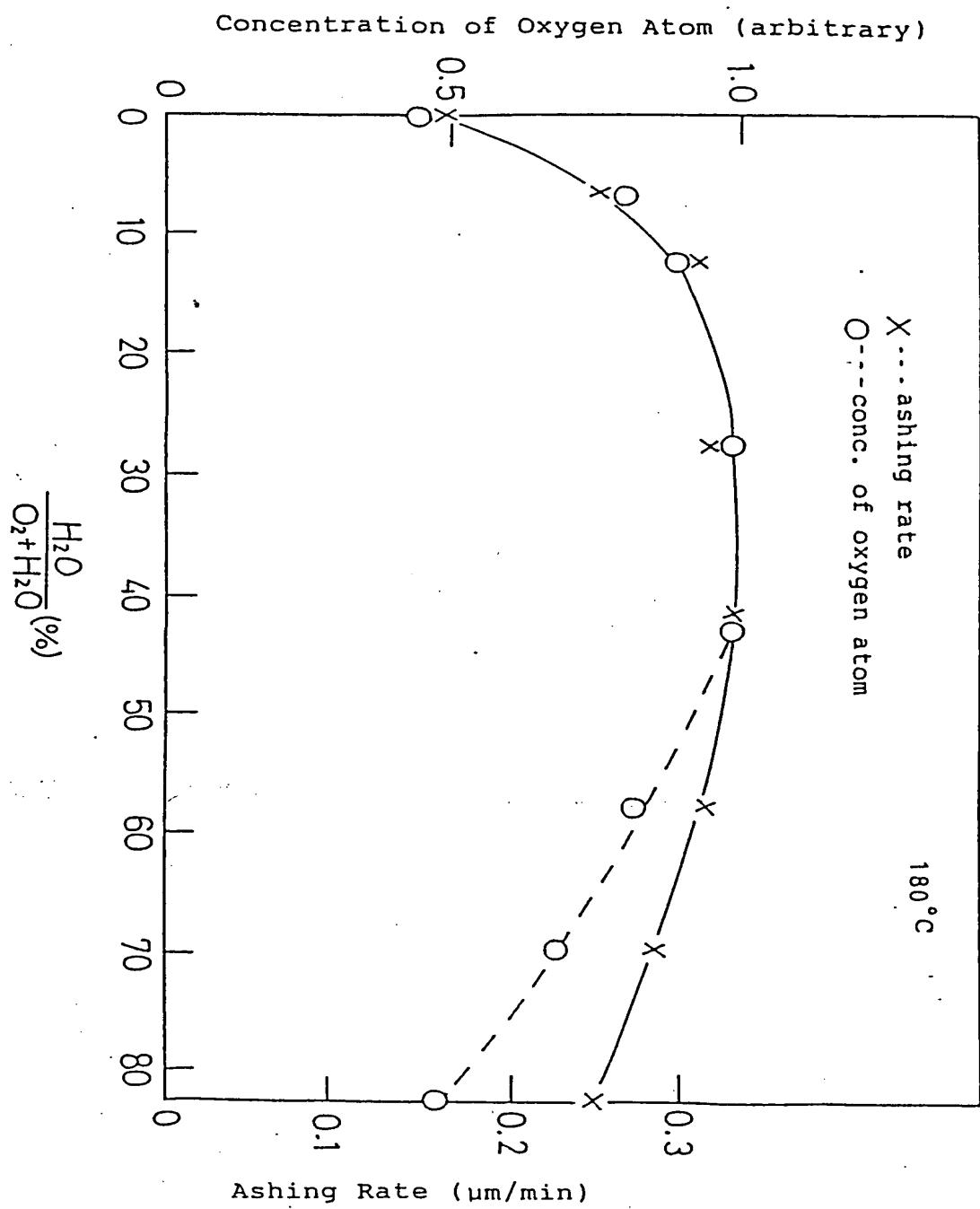


FIG. 3

FIG. 4



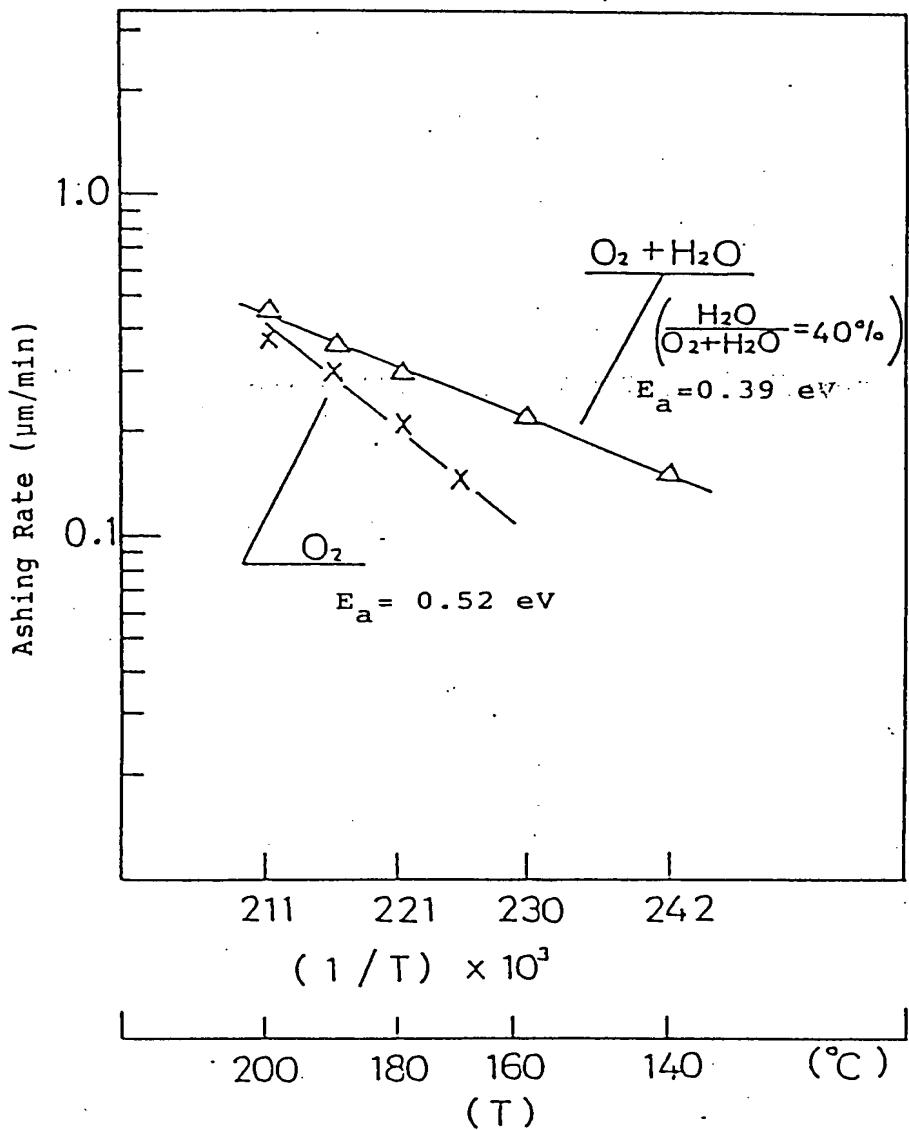


FIG. 5

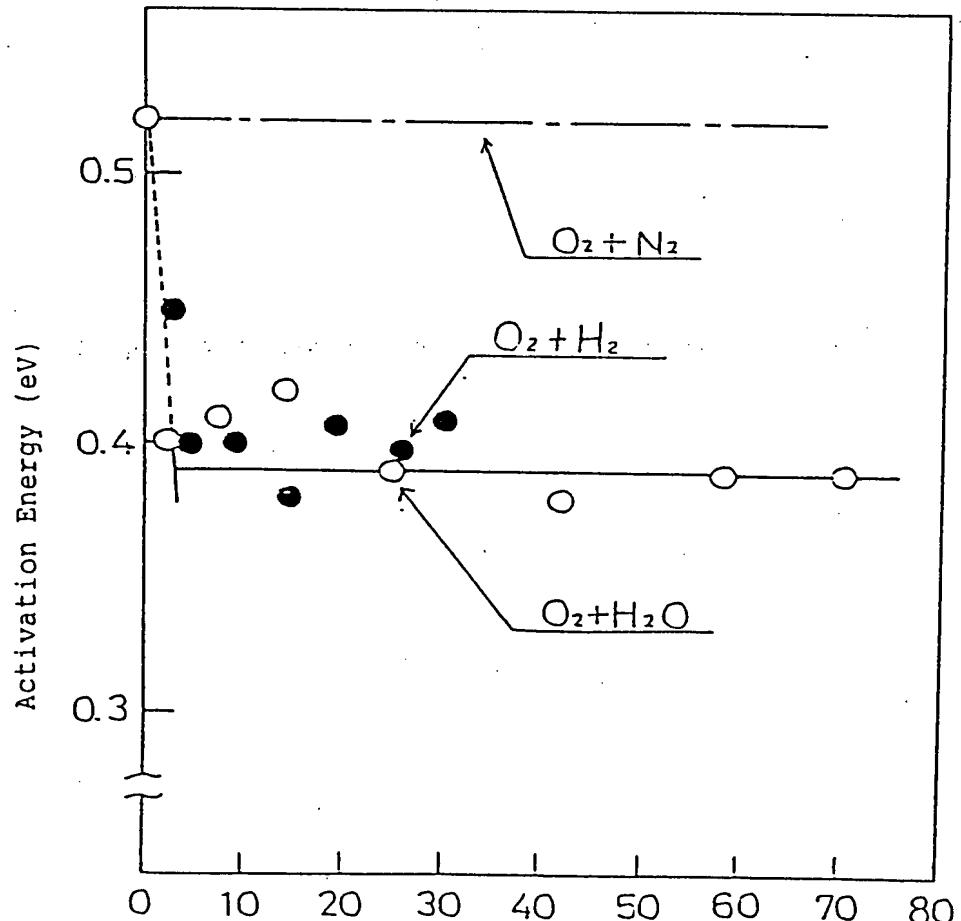


FIG. 6

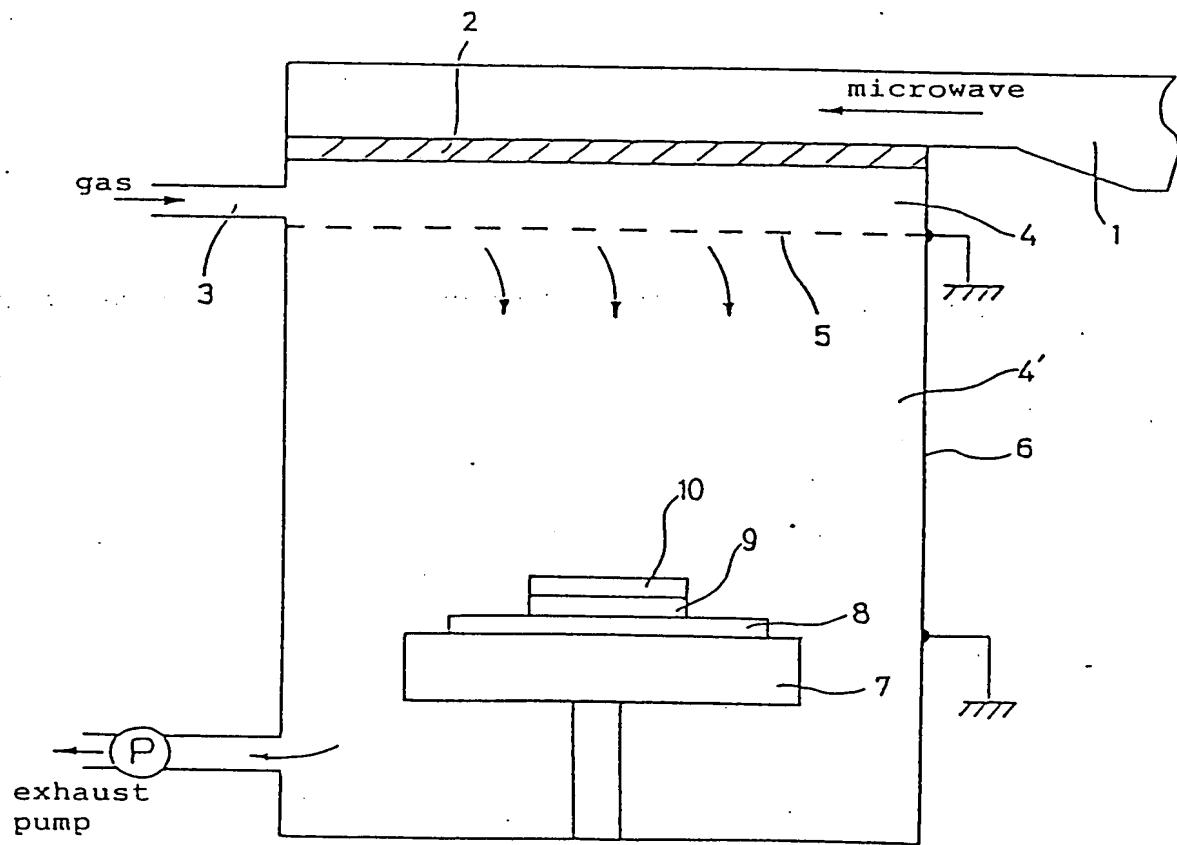


FIG. 7

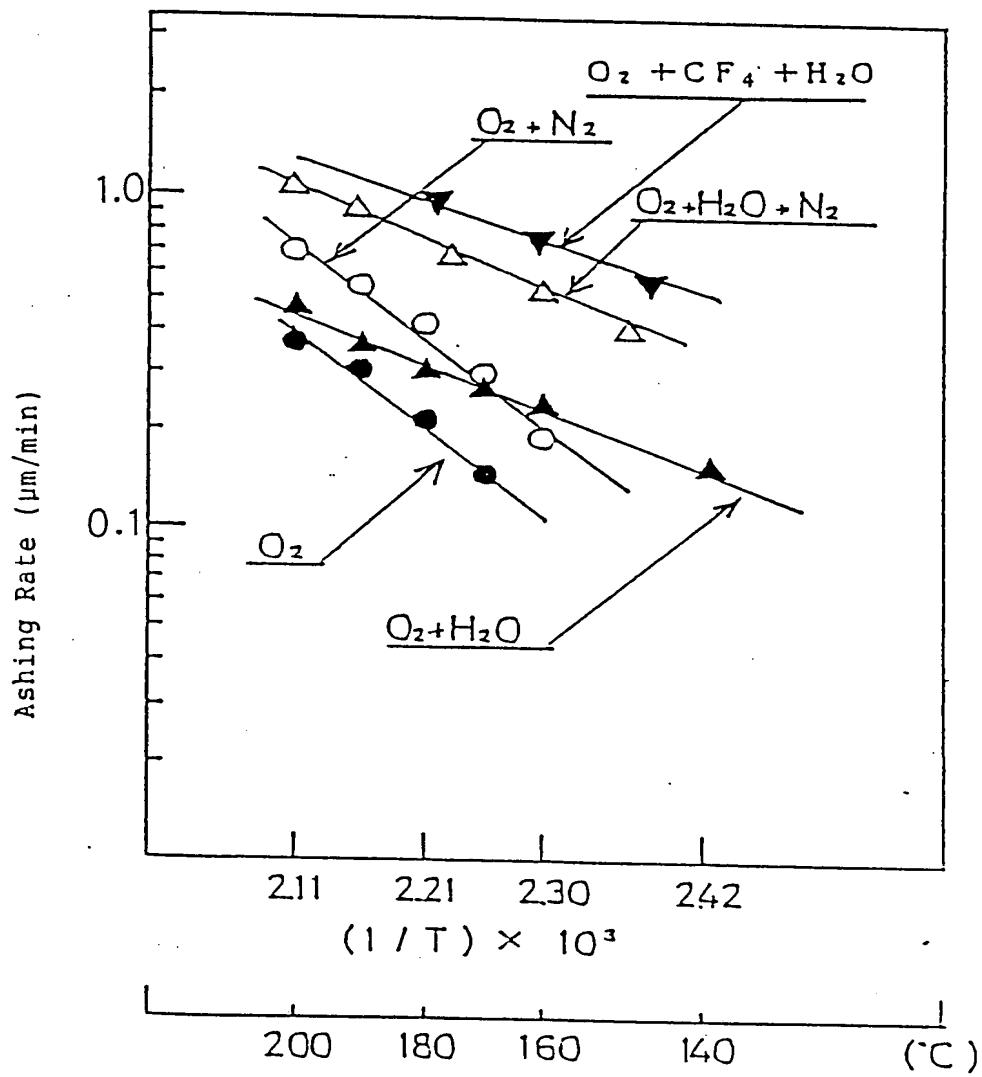


FIG. 8

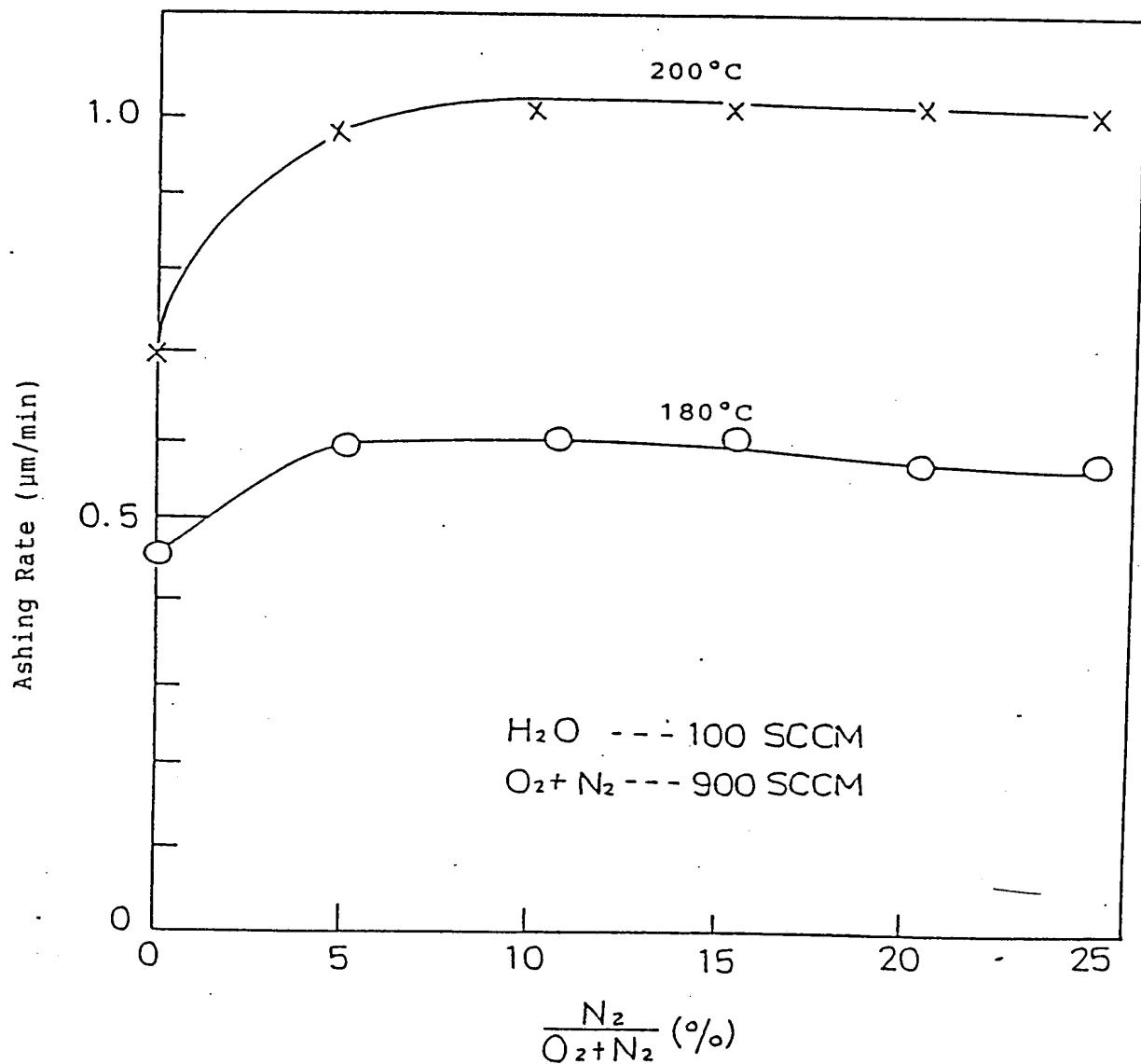


FIG. 9

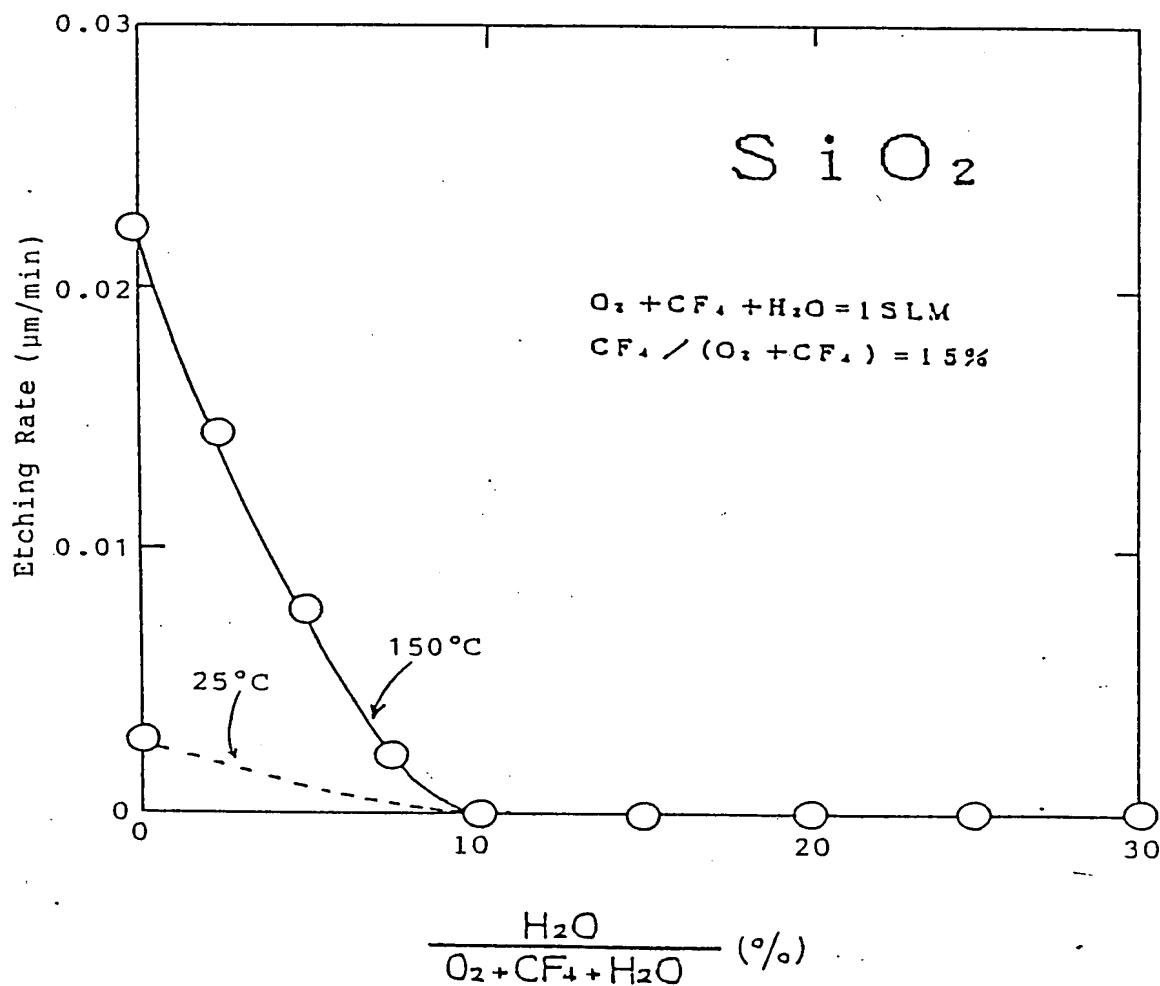


FIG. 10

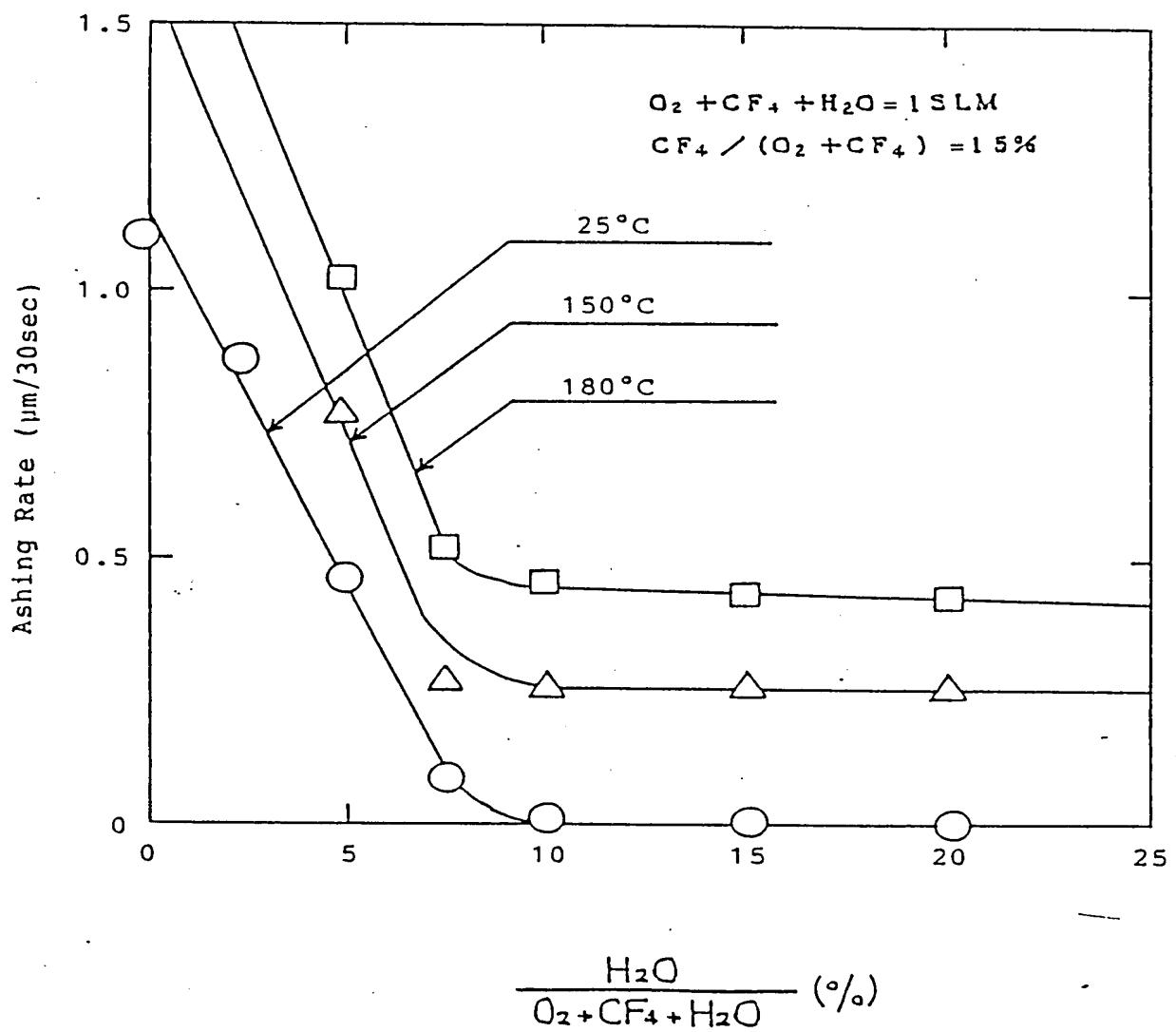


FIG. 11

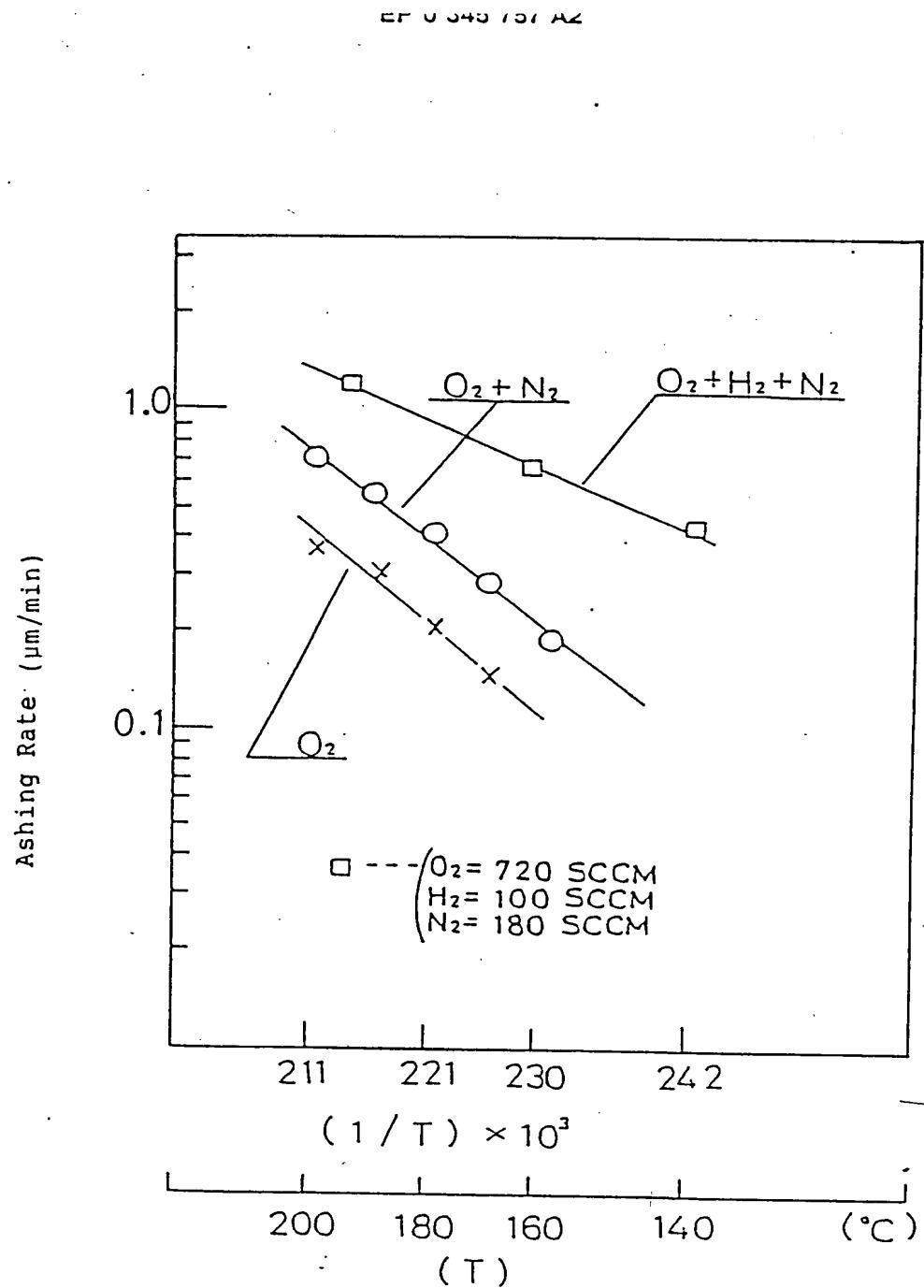


FIG. 12

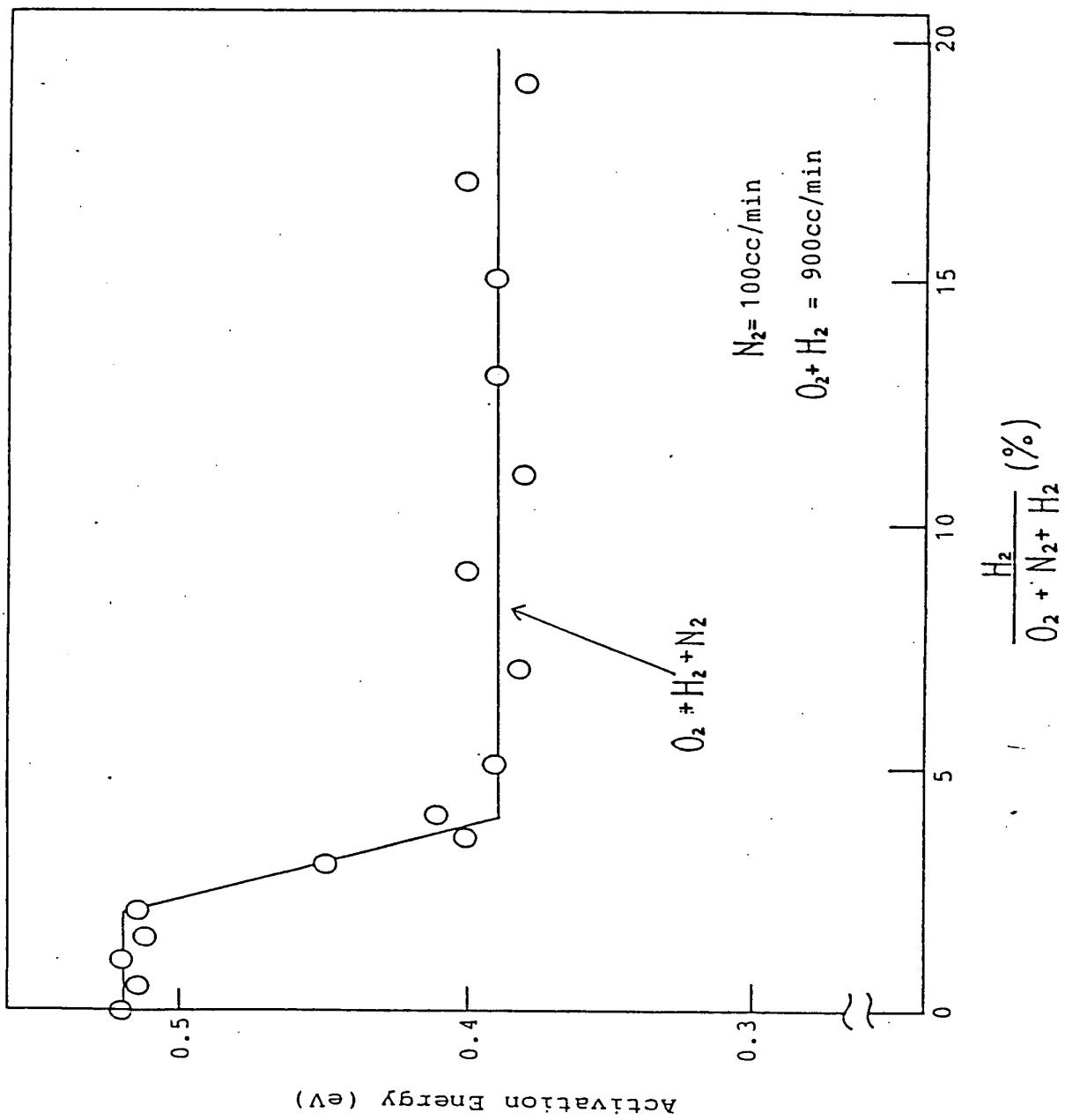


FIG. 13